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<b>13. ABSTRACT (Maximum 200 Words)</b> In recent years, supercritical (SC) CO <sub>2</sub> has been examined as an environmentally acceptable solvent for many processing applications. CO <sub>2</sub> has modest critical properties and is non-toxic, non-corrosive, and inexpensive. SC CO <sub>2</sub> has proven to be a very good solvent for a variety of polymers and copolymers. A collaborative effort between Johns Hopkins (JHU) Dept. of Chemical Engineering, JHU/Chemical Propulsion Information Agency (CPIA), and Army Research Lab (ARL) is examining the phase behavior and extraction of various binder polymers used in propellant, explosives, and pyrotechnic (PEP) formulations in SC CO <sub>2</sub> and other supercritical fluids for the purpose of developing environmentally acceptable processing and demilitarization methods for some current PEP materials, and for designing new PEP formulations that employ modified binder polymers amenable to SC CO <sub>2</sub> processing for enhanced life cycle pollution prevention. The polymers investigated include polyethylene, oxidized polyethylene, poly(vinylidene fluoride)-co-hexafluoropropylene) with trade names Viton-A and Fluorel, poly(urethane) with trade name Estane, poly(chlorotrifluoroethylene-co-vinylidene fluoride) with trade name Kel-F, and cellulose acetate butyrate.				
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# Supercritical Carbon Dioxide Based Processing of PEP Binder Polymers

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# SUPERCRTICAL CARBON DIOXIDE BASED PROCESSING OF PEP BINDER POLYMERS

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## ABSTRACT

In recent years, supercritical (SC) carbon dioxide ( $\text{CO}_2$ ) has been examined as an environmentally acceptable solvent for many processing applications. Carbon dioxide has modest critical properties and is non-toxic, non-corrosive, and inexpensive. Supercritical  $\text{CO}_2$  has proven to be a very good solvent for a variety of polymers and copolymers. A collaborative effort between The Johns Hopkins University (JHU) Department of Chemical Engineering, the JHU/Chemical Propulsion Information Agency (CPIA), and the Army Research Laboratory (ARL) is examining the phase behavior and extraction of various binder polymers used in propellant, explosives, and pyrotechnic (PEP) formulations in SC  $\text{CO}_2$  and other supercritical fluids for the purpose of developing environmentally acceptable processing and demilitarization (ingredient recovery) methods for some current PEP materials, and for designing new PEP formulations that employ modified binder polymers amenable to SC  $\text{CO}_2$  processing for enhanced life cycle pollution prevention. The polymers investigated include polyethylene (PE), oxidized polyethylene, poly(vinylidene fluoride-co-hexafluoropropylene) with trade names Viton-A (DuPont Company) and Fluorel (3M Corporation), poly(urethane) with trade name Estane (B.F. Goodrich Company), poly(chlorotrifluoroethylene-co-vinylidene fluoride) with trade name Kel-F (3M Corporation), and cellulose acetate butyrate (CAB 381-20). The solubilities of these polymers have been determined in pure  $\text{CO}_2$  and  $\text{CO}_2$  with cosolvents of ethanol and acetone at temperatures up to 300 °C and pressures up to 3000 bar. The results of this study show that SC  $\text{CO}_2$  processing has many potential applications related to life cycle pollution prevention goals with PEP materials. This paper will discuss the fundamental phase behavior of some binder polymers as well as briefly describe some possible applications in energetic materials processing.

## INTRODUCTION

Over the last several years, SC  $\text{CO}_2$  has been investigated for the extraction and recovery of valuable ingredients from various PEP material wastes. Table 1 shows representative PEP formulations with the respective energetic ingredients and binder polymers of interest in this program. Ingredients such as RDX, HMX, and TATB have very limited solubility in  $\text{CO}_2$  due to their polar nature (Morris, 1996). Magnesium powder is also not expected to be soluble in SC  $\text{CO}_2$ . This limited solubility has led to a strategy to directly extract the binder component of these materials using  $\text{CO}_2$  as a means to recover the more valuable ingredients. Another advantage of this process, relative to direct dissolution and recovery of the explosive ingredient using conventional solvent extraction methods, is that the extraction of the binder should leave the explosives particle size and morphology distribution unaffected, thereby enhancing the potential for the reuse of the ingredient in military PEP formulations without extensive requalification.

Another potential application of SC  $\text{CO}_2$  technology in the PEP industry that has received less attention is in the manufacturing cycle. In this area, organic solvent-free production of molding powders or extrusion feedstocks formed through the precipitation of  $\text{CO}_2$ -soluble binders onto appropriate particles can be envisioned. In this technique, polymer precipitation can be controlled through the reduction of pressure allowing precise control of the particle coating process. Research to gain an understanding of polymer precipitation from supercritical fluids on a molecular level is currently being performed at JHU.

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Table 1. Representative PEP Materials with Binders Studied

NAME	COMPONENTS
PBXN-5	HMX/VITON-A
PBXN-6	RDX/VITON-A
PBXN-201	RDX/VITON-A /TEFLON
PBX-9502	TATB/KEL-F 800
LX-17	TATB/KEL-F 800
MTV IGNITER	Mg/TEFLON/ VITON-A (FLUOREL)
IR FLARE	Mg/TEFLON/VITON-A
LOVA PROPELLANT	RDX/CAB/NC
COMP A-3	RDX/(PE or wax or ox-PE)
LX-14	HMX/ESTANE

#### SUPERCritical FLUID - POLYMER PHASE BEHAVIOR

Krukonis has shown that CO<sub>2</sub> at or near room temperature and at pressures typically below 600 bar can be used to solubilize a variety of polymeric oils, such as many polydimethyl and poly(phenylmethyl) silicones, perfluoroalkylpolyethers and chloro- and bromo-trifluoroethylene polymers (McHugh and Krukonis, 1993; Yilgor, et. al, 1984; Krukonis, 1985). Hoefling and coworkers have described the solubility of poly(perfluoropropylene oxide) and poly(dimethyl siloxane) in CO<sub>2</sub> (Hoefling, et al., 1991; 1992) and Xiang and Kiran (1995) have also reported on the high solubility of poly(dimethyl siloxane) in CO<sub>2</sub> at approximately 450 bar. It is also possible to dissolve very low molecular weight, slightly polar polymers, such as polystyrene or telechelic polyisobutylene, with molecular weights below 1,000 in supercritical CO<sub>2</sub> (Gregg, et al., 1994a; 1994b).

DeSimone and coworkers have generated a large body of work demonstrating that CO<sub>2</sub> can dissolve hydrocarbon polymers that contain fluorinated octyl acrylates and they have demonstrated the high solubility of poly(1,1-dihydroperfluoroctyl acrylate) (poly(FOA)) in supercritical CO<sub>2</sub> (see for example, Shaffer and DeSimone, 1995). In addition, they have developed interesting hydrocarbon-fluorocarbon block copolymers that also exhibit a high degree of solubility in CO<sub>2</sub> (Canelas, et al., 1996). Beckman and coworkers have also synthesized modest molecular weight block copolymers and graft copolymers that are CO<sub>2</sub> soluble (see for example, Hoefling, et al., 1993). Beckman and coworkers argue that the solubility of the copolymer depends in a somewhat complex manner on the number of fluorinated side groups and on the molecular weight of the side groups relative to the molecular weight of the hydrocarbon main chain. These studies demonstrate how creative, polymer synthetic chemistry can be used to improve polymer solubility in CO<sub>2</sub>.

The pressures and temperatures needed to dissolve a given polymer in CO<sub>2</sub> depend on the intermolecular forces in operation between solvent-solvent, solvent-polymer segment, and polymer segment-segment pairs in solution, and on the free volume difference between the polymer and CO<sub>2</sub>. Rather than present rigorous and complicated expressions for energetic and entropic interactions, approximate expressions are used here that reveal the important physical properties of both the polymer and CO<sub>2</sub> that govern whether a polymer will dissolve in CO<sub>2</sub>. Consider first the impact of intermolecular forces on solubility. A simplified expression shows how the intermolecular potential energy of an i-j pair of segments or molecules,  $\Gamma_{ij}$  depends on the physical properties of the polymer and the solvent (Prausnitz, et al., 1986).

$$\Gamma_{ij}(r) \approx -C_1 \frac{\alpha_i \alpha_j}{r^6} - C_2 \frac{\mu_i^2 \mu_j^2}{r^6 kT} - C_3 \frac{Q_i^2 Q_j^2}{r^{10} kT} - C_4 \frac{\mu_i^2 Q_j^2}{r^8 kT} - C_5 \frac{\mu_j^2 Q_i^2}{r^8 kT} + \text{complex formation} \quad (1)$$

where subscript  $ij$  represents  $\text{CO}_2$  and a segment of the polymer, the first term on the right-hand side, written in terms of the polarizabilities,  $\alpha_i$  represents dispersion interactions, the second term, written in terms of the dipole moments,  $\mu_i$  represents dipolar interactions, the third, fourth, and fifth terms, written in terms of the quadrupole moments,  $Q_i$  represent quadrupolar interactions, and the last term in this equation represents complex formation. In this equation  $r$  is the distance between the molecules,  $k$  is Boltzmann's constant,  $C_{1-5}$  are fixed constants, and  $T$  is absolute temperature. Neglected from equation (1) are expressions for induction interactions. Table 2 lists the properties of  $\text{CO}_2$ , ethanol, acetone, and chlorodifluoromethane (CDFM).  $\text{CO}_2$  has a modest critical temperature with a relatively high critical pressure. Due to its structural symmetry,  $\text{CO}_2$  does not have a dipole moment. But,  $\text{CO}_2$  does have a substantial quadrupole moment that operates over a much shorter distance than dipolar interactions. Kazarian and coworkers (1996) use spectroscopic techniques to characterize the interactions between  $\text{CO}_2$  and polymers. They demonstrate that the polymers possessing electron-donating functional groups (e.g., carbonyl groups) exhibit specific interactions with  $\text{CO}_2$ . They argue that this complex formation is most probably of a Lewis acid-base nature, where the carbon atom of the  $\text{CO}_2$  molecule acts as a proton donor and the carbonyl oxygen in the polymer as an electron donor. However, Kazarian and coworkers show that the strength of the  $\text{CO}_2$ -segment complex is generally less than 1 kcal/mol which makes it only slightly stronger than dispersion interactions. Therefore,  $\text{CO}_2$  polymer complex formation is not considered in the analyses of solubility data in the present study especially at elevated temperatures where complexing is expected to be reduced.

Table 2. Physical properties Solvents Used in this Study (Reid, et al., 1987).

	Critical Temperature (°C)	Critical Pressure (bar)	Critical Density (g/cm <sup>3</sup> )	Polarizability 10 <sup>25</sup> (cm <sup>3</sup> )	Dipole Moment (Debye)	Proton Acceptor (Donor)
$\text{CO}_2^*$	31.0	73.8	0.468	29.1	0	Donor
Ethanol	240.8	61.4	0.267	51.1	1.7	Acceptor & Donor
CDFM	96.2	49.7	0.522	67.3	1.4	Donor
Acetone	235.0	47.0	0.277	63.3	2.9	Acceptor

\* The quadrupole moment of carbon dioxide is  $-4.3 \cdot 10^{-26}$  erg<sup>1/2</sup> · cm<sup>5/2</sup>

The two cosolvents used in this study, ethanol and acetone, have significant dipole moments. Both ethanol and acetone have relatively large dielectric constants at room temperature, indicative of the polar nature of these solvents. The goal of using a cosolvent with  $\text{CO}_2$  is to create a mixed solvent which has modest critical properties as well as reasonable dielectric properties.  $\text{CO}_2$  has a very modest dielectric constant of about two regardless of temperature and pressure (Michels and Michels, 1933), but as shown in Table 2, it has a relatively low critical temperature. A number of studies have been done to determine the dielectric behavior of the  $\text{CO}_2$ -cosolvent mixtures to provide insight into the polar nature of these mixed solvent mixtures ranging from  $\text{CO}_2$  with argon (Drake and Smith, 1990) to methanol (Dombro et al., 1991; Roskar et al., 1992). In the alcohol studies the dielectric constant of the mixture increases with increasing solvent density as well as increasing alcohol mole fraction. Also, there appears to be no anomalous behavior of the dielectric constant near the respective mixture-critical points at each temperature. Ethanol is chosen as a cosolvent since it can hydrogen bond with hydroxyl and acid groups that appear in some of the polymers considered in this study. In addition, ethanol can hydrogen bond with itself. In contrast, acetone is a very polar cosolvent that can only accept a hydrogen, which means that it cannot hydrogen bond with itself.

It is important to remember that equation (1) is only a rough approximation to the more rigorous intermolecular potential energy function especially since the segmental motion of the polymer is constrained by the connectivity of the segments. Nevertheless, the approximate form of the intermolecular potential energy function provides a useful tool for interpreting experimental solubility data. From an energetic viewpoint, the relevant criteria of whether a polymer will dissolve in  $\text{CO}_2$  is fixed by the interchange energy of mixing  $i$ - $j$  pairs,  $\omega$ , given by

$$\omega = z [ \Gamma_{ij}(r, T) - \frac{1}{2} (\Gamma_{ii}(r, T) + \Gamma_{jj}(r, T)) ] \quad (2)$$

where  $z$  is the number of dissimilar solvent-segment pairs. Equations (1) and (2) provide insight as to why temperature plays such a dominant role in determining solubility. Equation (1) shows that polar forces and acceptor-donor complexing are more important at low-to-moderate temperatures because of their inverse temperature dependence. Due to the weak polar nature of  $\text{CO}_2$  the interchange energy is expected to be a sensitive function of temperature which means that polymer solubility will depend on temperature. The quadrupolar nature of  $\text{CO}_2$  works against it in solubilizing polymers that are predominantly comprised of nonpolar repeat units, since  $\text{CO}_2$  quadrupolar interactions dominate the interchange energy as the temperature is lowered. The polarizability of  $\text{CO}_2$ ,  $\alpha_{\text{CO}_2} = 27.6 \cdot 10^{-25} \text{ cm}^3$  is approximately equal to the polarizability of methane, a very weak supercritical fluid solvent. Conversely,  $\text{CO}_2$  will be shown to be a feeble solvent for polymers with repeat units that have large dipole moments since the interchange energy now favors polymer-polymer interactions rather than polymer- $\text{CO}_2$  interactions, especially at low temperatures where polar interactions are magnified.

Supercritical  $\text{CO}_2$  is highly compressible, so it is important to be aware of how its solvent power depends on its density. The internal energy of a mixture,  $U_{\text{mixture}}$ , depends in the following way on the density of the solvent for a homogeneous-isotropic solution.

$$\frac{U_{\text{mixture}}}{kT} \approx A_0 + A_1 \rho(P, T) \sum_{ij} x_i x_j \int \Gamma_{ij}(r, T) g_{ij}(r, T, \rho) r^2 dr \quad (3)$$

where  $g_{ij}(r, T, \rho)$  is the radial distribution function,  $A_0$  and  $A_1$  are constants,  $x_i$  is the mole fraction of component  $i$ , and  $\rho$  is the solvent density if the solution is moderately dilute in solute. This simplified formula suggests that the internal energy is directly related to density, which explains the heuristic that, to a first approximation, polymer solubility is proportional to  $\text{CO}_2$  density. However, this formula also shows why this heuristic is only true to a first approximation since the type and strength of interactions are buried in the  $\Gamma_{ij}(r, T)$  and  $g_{ij}(r, T, \rho)$  terms. Equations 1, 2, and 3 demonstrate that it is important to match the physical properties of  $\text{CO}_2$  with those of the polymer so that the interchange energy is of sufficient strength to insure finite polymer solubilities at a given pressure and temperature. However, if the interchange energy overwhelms the density effect, it is not possible to manipulate solubility by changing  $\text{CO}_2$  density with changes in the system pressure. Finally, equation 1 shows that if the temperature is varied, the interchange energy can be adjusted through the  $\Gamma_{ij}$ ,  $\Gamma_{ii}$ , and  $\Gamma_{jj}$  values to allow for the solubility of the polymer.

In addition to enthalpic considerations, the entropy of mixing is a very important, and often overlooked, consideration when assessing the possibility of polymer solubility in supercritical  $\text{CO}_2$ . The entropy of mixing is related to the free volume difference between the polymer and  $\text{CO}_2$ . Roughly speaking,  $\text{CO}_2$  must condense around the polymer in order to dissolve it. This condensation process represents a large entropy penalty that can dominate favorable enthalpic interactions and prevent the formation of a single phase. The entropy penalty increases as the chain backbone of the polymer molecule stiffens since  $\text{CO}_2$  must adopt highly constrained configurations to condense around a more rigid polymer. The rigidity of a polymer backbone is reflected in the value of the glass transition temperature ( $T_g$ ) of an amorphous polymer. Qualitatively, the entropy penalty paid by  $\text{CO}_2$  is related to the free volume of the polymer which is proportional to  $T - T_g$  (Armeniades, C. D.; Baer, 1977).

Table 3 gives the physical properties for the polymers used in this study. Polyethylene (PE) is soluble in a variety of supercritical fluid solvents including butane, butene, propane, propylene, ethane, and ethylene. Ethylene is the worst solvent for PE since its quadrupole moment produces a quadrupole-quadrupole interaction among ethylene molecules that is unfavorable for nonpolar polyethylene.  $\text{CO}_2$  also has a significant quadrupole moment which is roughly three times larger than the quadrupole moment of ethylene. For this reason,  $\text{CO}_2$  is also a poor solvent for nonpolar polyethylene. Studies have shown that PE can be dissolved in  $\text{CO}_2$  with the addition of a nonpolar cosolvent (Kiran and Xiong, 1993). Oxidized polyethylene is obtained by processing PE in an oxygen atmosphere where hydroxide, aldehyde, and acid groups have replaced some of the hydrogens along the polymer chain. The addition of these groups makes the polymer very polar and allows it to self associate.

Viton-A and Fluorel are both random copolymers of vinylidene fluoride (VDF) and hexafluoropropylene (VDF-HFP<sub>m</sub> where  $m$  denotes the mol% of hexafluoropropylene (HFP) in the backbone). Property data are not currently available for the Viton-A sample used in this study. Fluorel consists of 78 mole % VDF and 22 mole % HFP. Fluoropolymers of this type are soluble in most solvents containing a carbonyl group and insoluble in hydrocarbon and halogenated solvents. Fluorel dissolves in a number of polar solvents such as acetone, methyl ethyl ketone, cyclohexanone, and ethyl acetate. Looking at the copolymer structure, the difluoroethylene repeat unit should be slightly polar due to the charge density difference between the fluorine and the hydrogen molecules. The addition of a polar cosolvent, such as acetone, should significantly improve the solubility of this type of composition in SC  $\text{CO}_2$ .

Table 3. Physical properties of polymers used in this study.

	MW	M <sub>N</sub>	% Crystallinity	T <sub>g</sub> (°C)	T <sub>M</sub> (°C)	Possible Impurities
Polyethylene	108,000	20,100	37	- 123	113	---
Oxidized PE	3,600	1,300	---	---	---	---
Viton-A	---	---	---	- 27	---	<1% barium sulfate
Fluorel FC-2175	85,000		none	- 20	---	---
Kel-F 800	60,000 - 120,000	----	---	30	105	---
Kel-F 3700	~300,000 - 500,000	----	none	- 15	---	---
Estane 5703-FI/ 5702FI	~ 80,000	~ 15,000	---	- 31	~ 70	<5% talc or ca. stearate
CAB 381-20		70,000	semi to none	124-141	167-172	---

Kel-F 800 and Kel-F 3700 are both copolymers of chlorotrifluoroethylene and vinylidene fluoride (VDF-CTFE<sub>m</sub> where m denotes the mol% of chlorotrifluoroethylene (CTFE) in the backbone). Kel-F 800 contains 74 mol% chlorotrifluoroethylene and 26 mol% vinylidene fluoride and is a semi-crystalline copolymer which has a melting point of approximately 105 °C. Kel-F 3700 contains 31 mol% chlorotrifluoroethylene and 69 mol% vinylidene fluoride and is a non-crystalline copolymer. In pure supercritical CO<sub>2</sub> both copolymers are expected to be soluble at high to moderate pressures and at high temperatures.

Estane 5702-FI and 5703-FI are both thermoplastic rubbers based on an ABA block copolymer structure, where A blocks consist of aliphatic/aromatic polyurethane segments and B blocks consist of aliphatic polyester segments (Allen, 1993). The A blocks are rigid (hard blocks) and thus hold the polymer molecules in fixed arrangements at normal temperatures. The B blocks soften upon heating, however, thus providing some degree of flexibility to the polymer molecules at elevated temperatures. These polymers have initial molecular weights of approximately 80,000 with about 38% of the total attributable to the A blocks. The only significant difference between the 5702 and 5703 variations of the polymer is apparently the inclusion of different anti-caking agents - the 5702 formulation contains calcium stearate while the 5703 formulation uses talc.

The cellulose acetate butyrate (CAB) used in this study, designated 381-20, has one hydroxyl, four acetyl, and seven butyryl groups per four anhydroglucosidic units (Rancourt and Taylor, 1989). The number of hydroxyl groups in CAB has a large influence on its physical and solution properties since these hydroxyl groups can hydrogen bond with other hydroxyl groups on the same oligomer or on other oligomers.

## EXPERIMENTAL

### APPARATUS

Figure 1 shows a schematic diagram of the experimental apparatus used in this study. The main component is a high-pressure, variable-volume cell constructed of a high-nickel-content austenitic steel (Nitronic 50®, 5.7 cm o.d., 1.6 cm i.d. fitted with a 1.3 cm thick sapphire window) capable of operating to pressures of 3,000 bar. Typically, the polymer is loaded into the cell to within  $\pm$  0.002 grams. Then the cell is purged several times with N<sub>2</sub> and with the supercritical fluid solvent of interest at approximately 50 to 500 psi to remove traces of air. Liquid cosolvent is added with a syringe. The supercritical fluid solvent is then added to the cell to within  $\pm$  0.002 grams using a high-pressure bomb. The mixture in the cell is stirred using a magnetic stir

bar controlled by a magnet located beneath the cell. The contents of the cell are projected onto a video monitor using a camera coupled to a boroscope (Olympus Corporation, model F100-024-000-55) placed directly against the sapphire window.

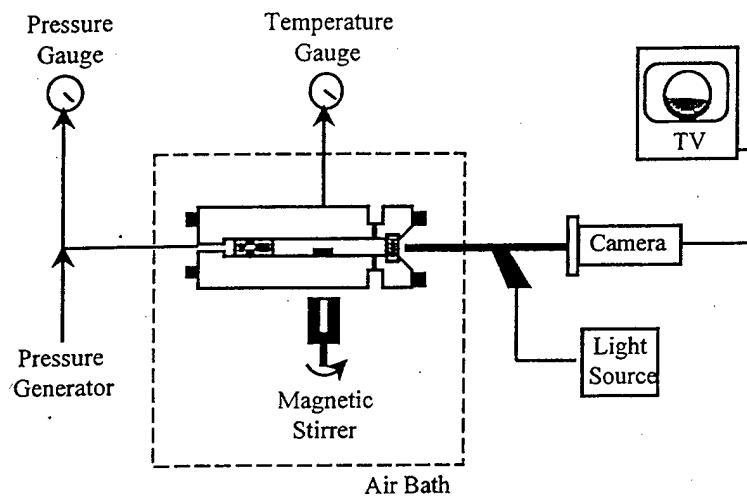
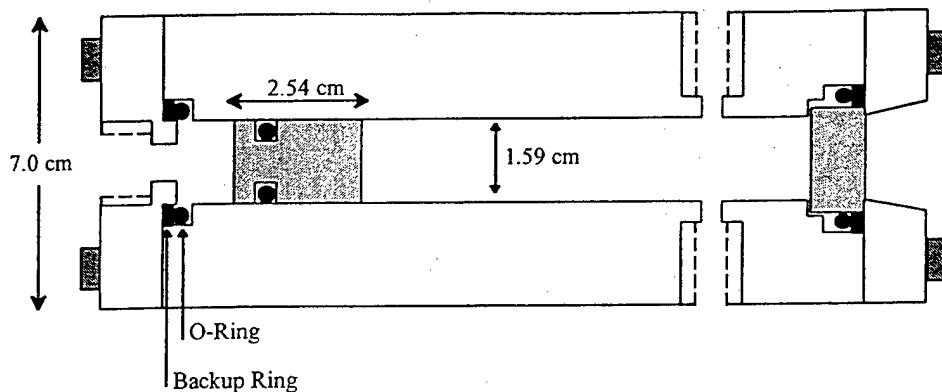


Figure 1. Schematic diagram of the view cell and experimental apparatus used in this study.

The solution is compressed to the desired pressure by moving a piston located within the cell. The piston is moved using water pressurized by a high-pressure generator (HIP Inc., model 37-5.75-60). Because the pressure is measured on the water side of the piston, a small correction (0.7 bar) is added to account for the pressure required to move the piston. The pressure is measured using a Heise pressure gauge (Dresser Ind., model CM-53920, 0 to 340 bar) accurate to within  $\pm 0.3$  bar. The system temperature, maintained to within  $\pm 0.2$  °C, is measured with a platinum-resistance device accurate to within  $\pm 0.2$  °C (Thermometrics Corp., Class A) placed in a thermowell on the surface of the cell.

#### TECHNIQUES

Figure 2 shows a schematic representation of a cloud-point curve which is used to characterize the solubility of a polymer in a supercritical fluid solvent. The pressure is raised at constant temperature until one phase is observed. The pressure is then lowered to determine the threshold at which two phases begin to appear. The cloud point pressure is defined as the point at which the solution becomes so opaque that it is no longer possible to see the stir bar in solution. Cloud points obtained in this manner are identical to those defined as the point where there is a 90% drop in transmitted light through the solution. Cloud point measurements are repeated at least twice at each temperature and are typically reproducible to within  $\pm 10$  bar.

The cloud point data are obtained at a constant concentration of polymer in solution. In this study, cloud point results were obtained at a polymer concentration of about 5 weight percent. A typical pressure-composition (P-x) isotherm for a polymer-solvent system is flat in the concentration range between ~5 and ~15 wt% polymer (Allen and Baker, 1965; Irani and Cozwith, 1986; Lee, et al, 1994). Thus, it is not particularly important that the concentration of polymer in solution be precisely the same in every experiment.

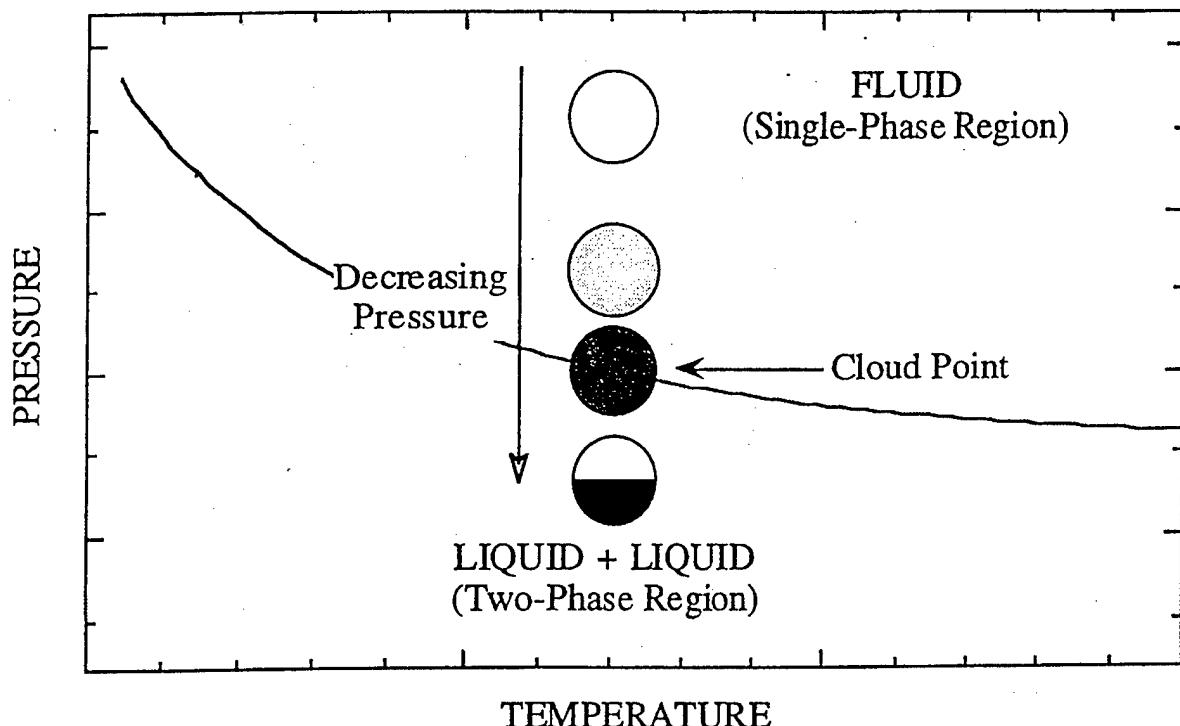


Figure 2. Schematic depiction of a pressure-temperature (P-T) cloud-point curve for a polymer-solvent system.

## EXPERIMENTAL RESULTS

### POLYETHYLENE (PE) AND OXIDIZED PE

PE was determined to be insoluble in  $\text{CO}_2$  up to temperatures of 290 °C and pressures of 2,475 bar. The poor solvent power of  $\text{CO}_2$  for PE becomes readily apparent by considering the solubility of low molecular weight nonpolar hydrocarbons in  $\text{CO}_2$  as shown in Figure 3. Octane and  $\text{CO}_2$  have a continuous critical-mixture curve that extends between the two pure component critical points. However, if the molecular weight of octane is doubled to hexadecane, the critical-mixture curve is shifted to higher pressures and the low temperature branch of the curve exhibits a steep rise in slope near 30 °C. At these cold temperatures the resultant phase behavior is usually attributed to enthalpic interactions. Evidently, the sharp rise in the critical-mixture curve is a consequence of a large energy mismatch between  $\text{CO}_2$  and hexadecane -- that is, the interchange energy,  $\omega$ , is dominated by  $\text{CO}_2$ - $\text{CO}_2$  quadrupolar interactions rather than  $\text{CO}_2$ -hexadecane dispersion or induction interactions. In other words,  $\text{CO}_2$  is too polar for hexadecane once the temperature is reduced below 30 °C since  $\text{CO}_2$ - $\text{CO}_2$  quadrupolar interactions scale with inverse temperature. If the molecular size of the nonpolar hydrocarbon is approximately doubled again to a C<sub>30</sub> molecule, the critical-mixture is shifted to higher pressures and the sharp rise in the curve occurs at 60 °C. Extrapolating the results shown in Figure 3 to PE, a branched hydrocarbon with approximately 1,400 CH<sub>2</sub> groups, it is apparent that  $\text{CO}_2$  is too polar for PE even at temperatures in excess of 290 °C. Therefore, a polymer or copolymer needs some polarity before it will exhibit any solubility in  $\text{CO}_2$ . However, hydrocarbon waxes of low molecular weight, similar to those investigated for some explosives compositions (Kaye and Herman, 1983), should readily dissolve in SC  $\text{CO}_2$ .

Not surprisingly oxidized PE also does not dissolve in pure  $\text{CO}_2$ . Oxidized PE has hydroxyl, carbonyl, aldehyde, and acid groups along the chain backbone which makes this polymer polar and allows the polymer to hydrogen bond to itself and to other oligomers.  $\text{CO}_2$  is just too weak a solvent to overcome the strong hydrogen bonding between polar sites in oxidized PE. However, Figure 4 shows that oxidized PE is soluble in  $\text{CO}_2$  if ethanol or acetone is used as a cosolvent. Unfortunately,

extremely high temperatures are needed to dissolve oxidized PE even in the presence of a cosolvent. These temperatures are outside of safe processing limits for most energetic materials.

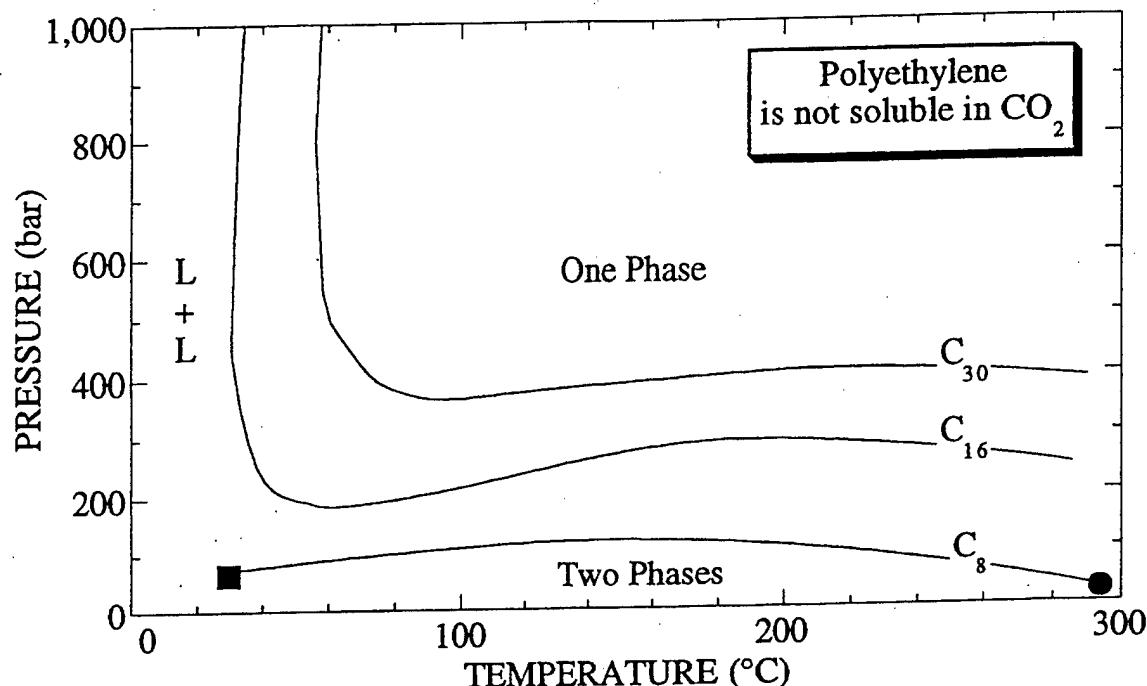


Figure 3. Critical-mixture curves for octane ( $C_8$ ), hexadecane ( $C_{16}$ ), and squalane ( $C_{30}$ ) obtained by Liphard and Schneider (1975). The closed square represents the critical point of  $CO_2$  and the closed circle is the critical point of octane.

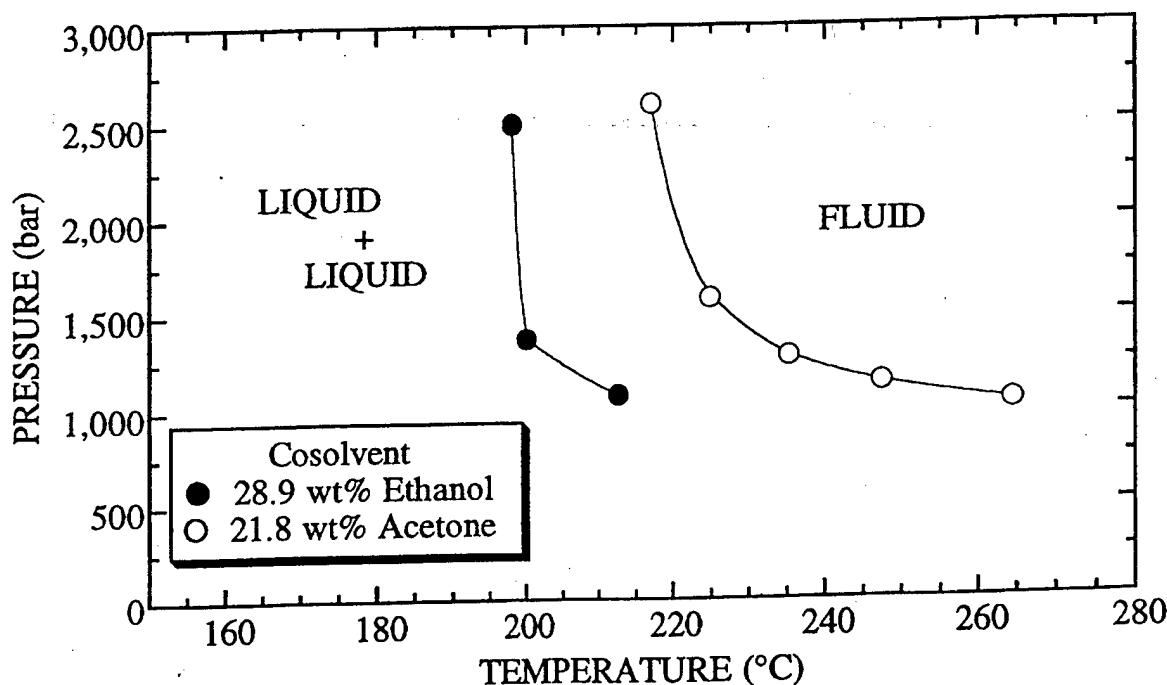


Figure 4. Cloud-point behavior of oxidized polyethylene in  $CO_2$  with ethanol and acetone obtained in this study.

## VITON-A AND FLUOREL

Viton-A is used in some explosive formulations as well as in igniter compositions and IR decoy flares. Fluorel is a qualified replacement material for Viton-A in some igniter compositions (Nauflett, 1996). Fluorel and Viton-A are statistically random copolymers of approximately 22 mol% hexafluoropropylene (HFP) with vinylidene fluoride (VDF-HFP<sub>22</sub>) where the subscript on HFP indicates the mole fraction of HFP in the copolymer. These are amorphous copolymers that are more flexible than poly(vinylidene fluoride) which suggests that there should only be a modest entropy penalty for dissolution in CO<sub>2</sub>. Although Viton-A and Fluorel have been determined to be quite similar (Nauflett, 1996) by the Naval Surface Warfare Center/Indian Head, Maryland (NSWC/IH), dramatic differences in the phase behavior of Viton-A and Fluorel with CO<sub>2</sub> were observed in this study.

Figure 5 shows that Fluorel (VDF-HFP<sub>22</sub>) does dissolve in pure CO<sub>2</sub>. The data indicate the feasibility of processing Fluorel-based Viton-A analogs of PEP formulations in SC CO<sub>2</sub> at safe temperatures. Organic solvent free manufacture of explosives molding powders and igniter extrusion feedstock are two possible examples. In addition, the data show that recovery of valuable ingredients from Fluorel based materials would be possible for future demilitarization considerations.

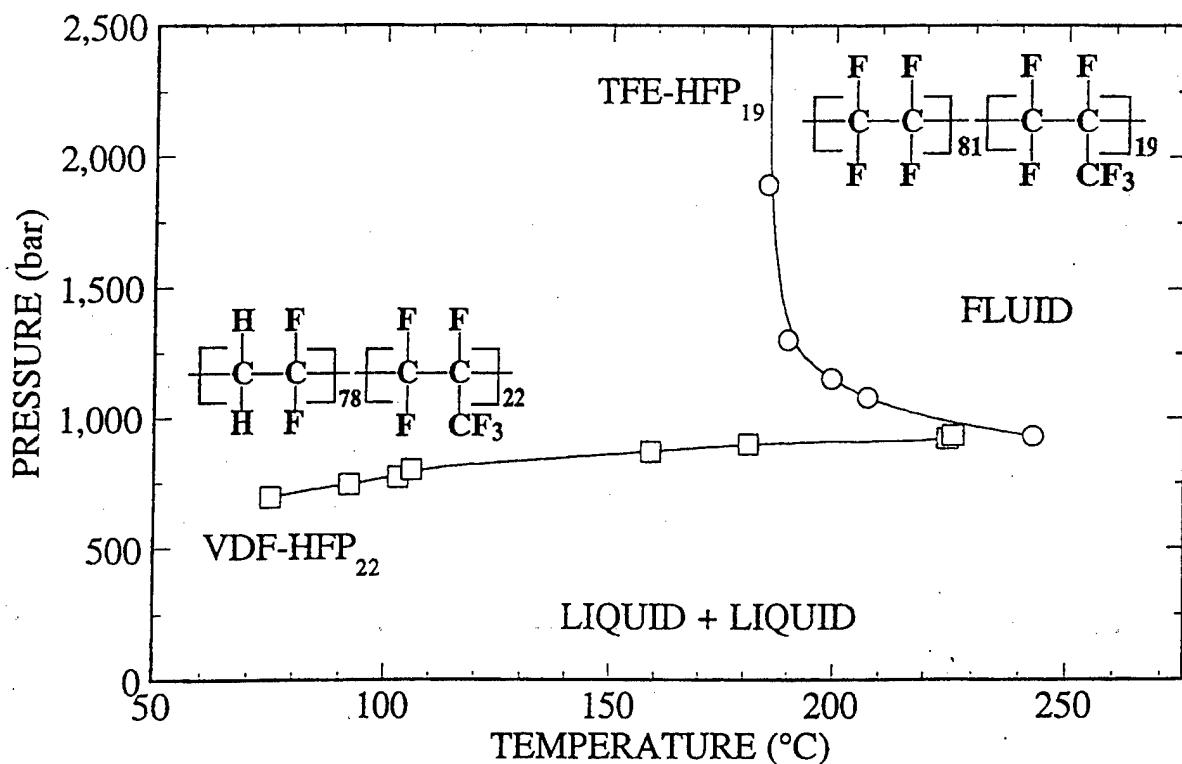


Figure 5. Comparison of the poly(tetrafluoroethylene-co-hexafluoropropylene) (TFE-HFP<sub>19</sub>) and poly(vinylidene fluoride-co-hexafluoropropylene) (VDF-HFP<sub>22</sub>) cloud-point curves in CO<sub>2</sub>. The TFE-HFP<sub>19</sub> cloud-point data are obtained by Mertdogan, et al., 1996.

Two distinct phases were observed even to temperatures of 284 °C and pressures of 2,200 bar for the CO<sub>2</sub>/Viton-A system. In additional experiments, the Viton-A was washed with HCl and water or dissolved in acetone and filtered, respectively, to remove any impurities or additives that could mask the true phase behavior. Even with these two different pretreatment steps, two phases were observed with pure CO<sub>2</sub>. Similar observations were obtained in SC CO<sub>2</sub> with 24.9 wt% acetone cosolvent. On the other hand, the Viton-A sample could be completely dissolved in pure acetone at room temperature.

The differences in phase behavior between Viton-A and Fluorel could be attributed to different functional end groups on the polymeric chains of the respective compositions or to the presence of additives in the materials. Unlike Fluorel, the Viton-A used in this study is coated with a partitioning agent for packing purposes. Small amounts of an impurity or additive

could mask the visual phase behavior obtained in the experiments. Additional work including supercritical fluid fractionation experiments could be performed to gain insight into the fundamental reasons for the observed behavior. In addition, since manufacturing processes for Viton-A have varied over the years, further study is required to determine if other variants of Viton-A might be soluble in SC CO<sub>2</sub>.

The ideal nature of the VDF-HFP22 binder composition, with respect to SC CO<sub>2</sub> processing, is illustrated by examining the results of slight modifications of the polymer structure. In a related study by Rindfleisch, et al. (1996), it is shown that CO<sub>2</sub> does not dissolve poly(vinyl fluoride), poly(vinylidene fluoride), and poly(tetrafluoroethylene) even at temperatures of 300 °C and pressures of 2,750 bar. Figure 5 also shows a comparison of the cloud-point behavior of Fluorel (VDF-HFP22) in CO<sub>2</sub> to that found with poly(tetrafluoroethylene-co-hexafluoropropylene) (TFE-HFP19) in CO<sub>2</sub> obtained at JHU by Mertdogan and coworkers (1996). Both copolymers are statistically random with approximately 20 mol% hexafluoropropylene (HFP) in the backbone; however, two hydrogen atoms of the VDF group are replaced with fluorine atoms in the TFE-HFP19 composition. There are dramatic differences in the location of these two cloud-point curves. Both cloud-point curves virtually superpose at temperatures in excess of 210 °C. The nonpolar TFE-HFP19 curve has a very sharp increase in pressure at temperatures near 185 °C. The sharp pressure rise in the TFE-HFP19-CO<sub>2</sub> cloud-point curve is a result of "hot" CO<sub>2</sub> being too polar to dissolve this nonpolar copolymer. In contrast, the VDF-HFP22 curve exhibits a slightly positive slope down to temperatures near 100 °C. The major difference between these two copolymers is that VDF in Fluorel has a dipole moment that makes it energetically more favorable to remain in solution in CO<sub>2</sub> as the temperature is lowered and polar forces increase.

The addition of small amounts of acetone (5%) as a cosolvent reduces the pressure threshold for dissolution of Fluorel in CO<sub>2</sub>. As shown in Figure 6, the cloud-point pressures of the Fluorel-CO<sub>2</sub>-acetone system can be further reduced to very low pressures with increased amounts of acetone added to the mixture. In addition to the direct polymer processing applications which are the subject of this study, understanding of this phase behavior is important to identifying optimum processing parameters for a new Fluorel-based Magnesium-Teflon-Viton (MTV) pyrotechnic crumb manufacturing technique being investigated by Farncomb and Nauflett of NSWC/IH. In this process, SC CO<sub>2</sub> is being examined as an anti-solvent in place of hexane to precipitate dissolved Fluorel from a slurry of magnesium and Teflon in acetone (Farncomb and Nauflett, 1996).

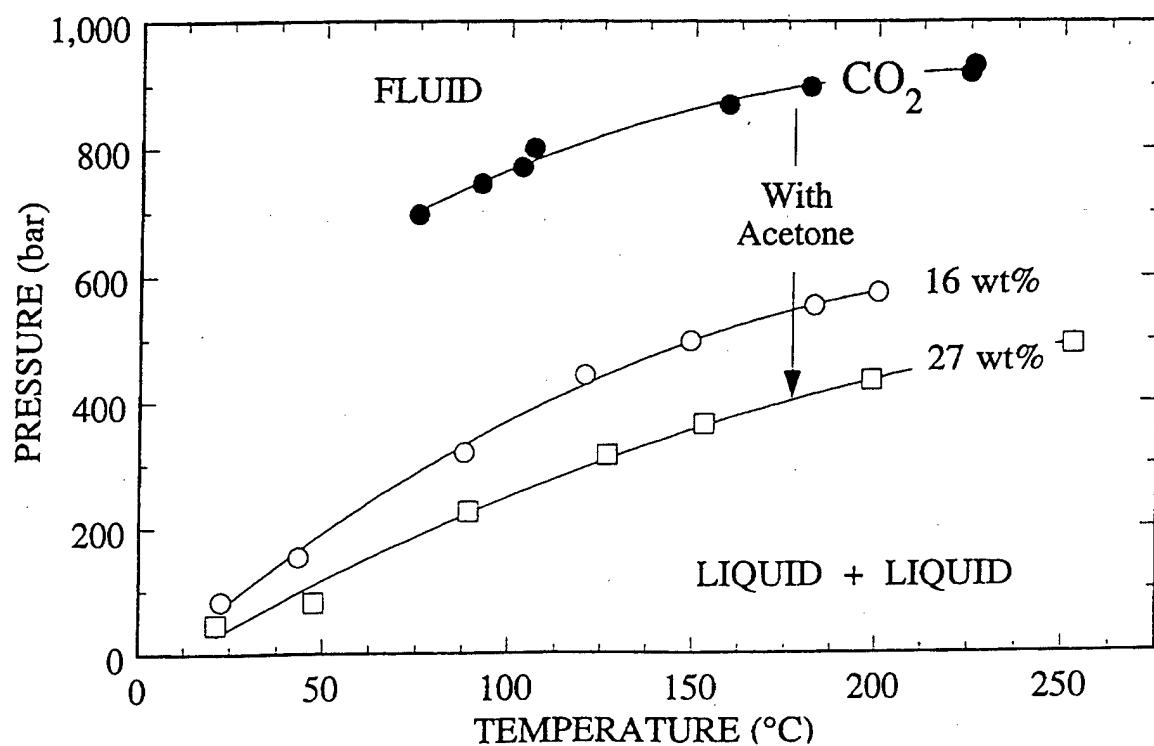


Figure 6. Cloud-point curves for Fluorel in pure CO<sub>2</sub> and in CO<sub>2</sub>-acetone mixtures (containing higher levels of acetone) obtained in this study (DiNoia et. al, 1996).

## KEL-F 800 AND KEL-F 3700

Kel-F 800, poly(chlorotrifluoroethylene-co-vinylidene fluoride) with 74 mol% CTFE and 26 mol% VDF (CTFE-VDF26) dissolves in pure  $\text{CO}_2$  and in  $\text{CO}_2$ -acetone mixtures. Figure 7 shows the cloud-point curves for these systems. The cloud-point curve has a characteristic trend found with similar type solutes in  $\text{CO}_2$ . The curve rapidly increases to high pressures at approximately of 140 °C, which is 35 °C above the melting point of Kel-F 800. Solid Kel-F 800 was not seen in solution. The shape of the Kel-F 800 cloud-point curve has the same characteristics of that found with a similar fluoroelastomer, TFE-HFP19 in  $\text{CO}_2$  as shown in Figure 5. Addition of a polar cosolvent such as acetone was also very effective in reducing the cloud-point threshold for Kel-F 800. The addition of 10 wt% acetone to  $\text{CO}_2$  lowers the cloud-point curve by approximately 1,000 bar. Relative to the pure  $\text{CO}_2$  curve, the  $\text{CO}_2$ -acetone curve also increases in pressure as the temperature is lowered, but the increase occurs at 30 °C lower temperature. Adding more acetone to the mixture will reduce the pressures needed to obtain a single phase. Notice also that the Kel-F 800- $\text{CO}_2$ -acetone curve does not have such an extreme increase in pressure as the temperature is lowered. Evidently, favorable acetone-Kel-F 800 polar interactions help lower the cloud-point pressures as the temperature is lowered. These data indicate the feasibility of processing Kel-F 800 based formulations, particularly those containing highly stable energetic ingredients, using a SC  $\text{CO}_2$  process with minimal organic solvent. Again, possible applications include manufacture of molding powders and extrusion feedstock, and ingredient recovery from existing Kel-F based materials.

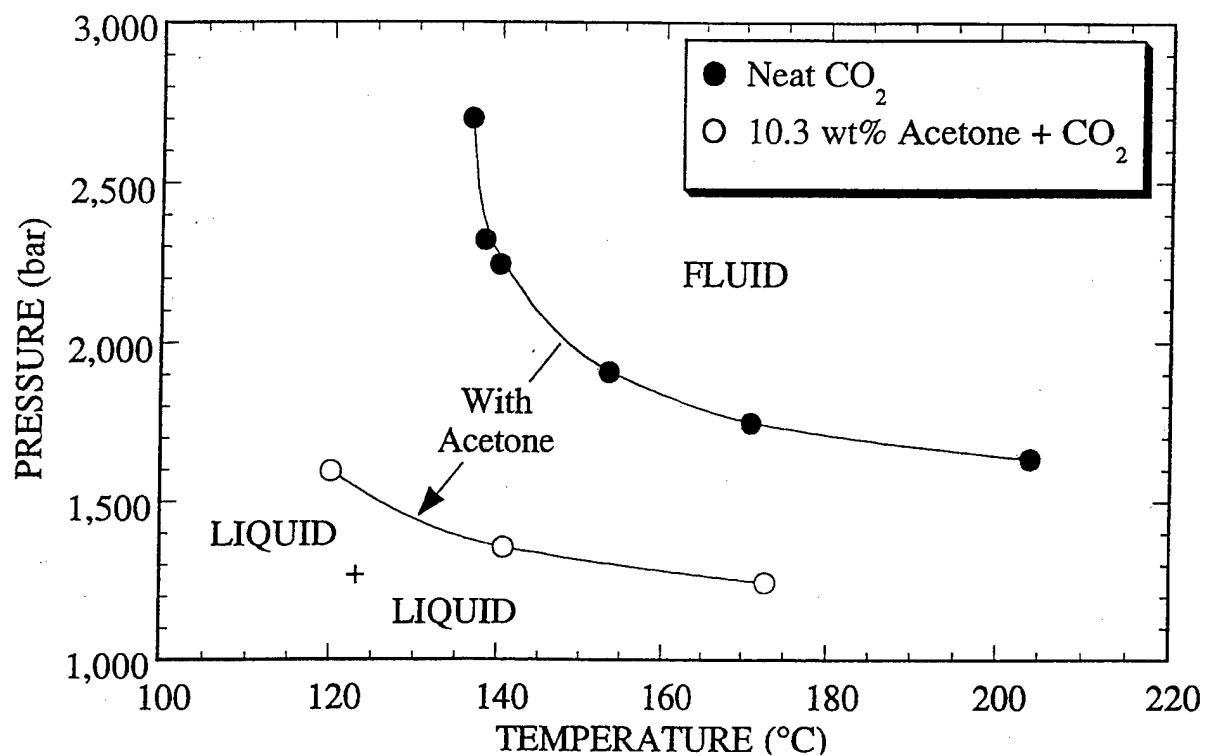


Figure 7 Cloud-point curves for Kel-F 800, poly(chlorotrifluoroethylene-co-vinylidene fluoride) in pure  $\text{CO}_2$  and a  $\text{CO}_2$ -acetone mixture obtained in this study.

Subsequently, the ability to recover valuable explosives ingredients from Kel-F 800 based formulations with a reduced solvent, SC  $\text{CO}_2$  based process has been successfully demonstrated in laboratory scale extractions at ARL using both an inert plastic bonded explosive formulation and live PBX-9502 samples. In the inert experiments, a sugar/Kel-F 800 formulation was prepared by adding sugar to a mix of Kel-F 800 in acetone. The sugar was reduced to about 300 micron particle size. The acetone was allowed to evaporate while the mixture was stirred using a teflon-coated stir bar. The composition of the dried sugar/Kel-F 800 mix was about 9-10% Kel-F 800. About 200 mg of the sample formulation was loaded into an approximately 0.5 ml supercritical fluid extraction vessel. The vessel was weighed empty, before extraction, and after extraction. In each case, a mass loss was observed following extraction at 150 °C and pressures between 7500 and 10000 psi with  $\text{CO}_2$ /acetone mixtures

containing varying amounts of acetone. The mass loss was not consistent, indicating (among other things) probably an inconsistency of the Kel-F 800 coating on the sugar sample - this is not too surprising considering the manner in which the sample was prepared. Following the extractions, the sugar was removed from the vessel and dissolved in about 5 ml water. Polymer residue was quite visible in runs 1 and 2, but only trace amounts were seen in run 3. Results from the inert material extractions were as follows:

Run	T(°C)	P(PSI)	% (wt) Acetone	Results
1	150	7500	19	partial removal of Kel-F 800
2	150	10000	19	partial removal of Kel-F 800
3	150	10000	32	full removal of Kel-F 800

Following these experiments, extractions of live PBX-9502 samples were performed. The PBX-9502 formulation contains about 5% Kel-F 800. Samples were prepared by pressing a molding powder of the composition into 0.25 inch diameter by approximately 0.5 inch long pellets with a nominal mass of 0.5 gram. Results from PBX-9502 extractions were as follows:

Run	T(°C)	P(PSI)	% (wt) Acetone	Vessel size	Result
4	150	10000	34	7.5 ml	little mass loss
5	150	10000	34	0.5 ml	~ 8% mass loss, sample powdered

In run 4, a larger vessel containing a full 0.5 gram sample was used and the extraction appeared to be unsuccessful. A possible explanation for this result is that incomplete thermal equilibration may have occurred (the vessel was not really at 150 °C). In run 5, a 250 mg sample was extracted using the smaller vessel (used for the inert extractions). In order to use the smaller vessel, the sample was partially cut and crushed. In this case, a mass loss consistent with the removal of the Kel-F 800 polymer was observed and a powdered residue was recovered. The recovery of what appears to be powdered TATB, along with the observed mass loss, is presumably evidence of successful binder extraction. Since the TATB explosive recovered is insoluble in just about every solvent except for sulfuric acid, no attempt was made through visual observation to determine the presence of residual polymer impurity in the recovered TATB. Additional work to determine the purity of the recovered TATB, as well as to repeat the experiment in the larger vessel using an oven to ensure thermal equilibration would be beneficial.

Again by examining a modification of the polymer structure, the desirability of Kel-F 800 binder with respect to CO<sub>2</sub> processing is apparent. Kel-F 3700, poly(chlorotrifluoroethylene-co-vinylidene fluoride) with 31 mol% CTFE and 69 mol% VDF (CTFE-VDF69) does not dissolve in pure CO<sub>2</sub>. Kel-F 3700 is more polar than Kel-F 800 since it contains a larger percentage of polar vinylidene fluoride repeat units. In addition, Kel-3700 did not dissolve in CO<sub>2</sub> with 22 wt% acetone, although Kel-F 3700 dissolved in pure acetone at room temperature. The reason for this discrepancy is not known at this time. However, additional experiments could be performed to examine this issue further by determining whether poly(chlorotrifluoroethylene) dissolves in pure CO<sub>2</sub> and in CO<sub>2</sub> plus acetone.

#### ESTANE 5703

Estane 5703 could not be dissolved in pure CO<sub>2</sub> from room temperature to 250 °C and pressures as high as 2,449 bar. Since Estane is soluble in acetone at room temperature, it might be expected to be soluble in SC CO<sub>2</sub> with some level of acetone cosolvent. These experiments could be the subject of future work. Since aliphatic polyesters are known to undergo hydrolytic degradation at ordinary conditions of temperature and humidity (Allen, 1993), another interesting experiment might be to attempt to hydrolyze the binder with small amounts of water in SC CO<sub>2</sub> as a means to recover valuable energetic ingredients from Estane based formulations.

#### CELLULOSE ACETATE BUTYRATE (CAB 381-20)

CAB could not be dissolved in pure CO<sub>2</sub> or in CO<sub>2</sub> with ethanol or CDFM cosolvents at room temperature to 85 °C and pressures as high as 1,245 bar. Even when operating at very high pressures it was not possible to obtain a single clear phase. The solution with the cosolvents added to the CO<sub>2</sub> looked very dark suggesting that a small amount of the CAB was soluble in the mixture. The slight solubility of some CAB oligomers suggests that SC CO<sub>2</sub> fractionation of CAB might prove interesting as a raw materials purification or optimization step in LOVA gun propellant manufacture. Beaupre et al. (1991) have observed some lot-to-lot variability of CAB binder materials, possibly due to variations in both hydroxyl and ester substitution, which could result in performance variations. The lack of solubility is more than likely a result of the high hydroxyl content of CAB

381-20 rather than its high molecular weight since it has been demonstrated that CO<sub>2</sub> can dissolve very high molecular weight polymers if the intermolecular interactions between CO<sub>2</sub> and the segments of the polymer are favorable (McHugh and Krukonis, 1993). On the other hand, formulations such as CAB 551-0.2, with a higher butyrate content and lower molecular weight which lowers the glass transition and melting temperatures, could possibly show solubility in CO<sub>2</sub>-cosolvent mixtures. This could be considered in future environmentally friendly LOVA gun propellant development programs.

## CONCLUSIONS AND RECOMMENDATIONS

The results of the study indicate that processing of select PEP binder polymers in supercritical carbon dioxide is possible in accordance with life cycle pollution prevention initiatives to eliminate or at least minimize the use of organic solvents. Partially halogenated copolymers appear to be particularly amenable to SC CO<sub>2</sub> processing. Immediate potential applications may include the separation and recovery of valuable ingredients from Fluorel (vinylidene fluoride-hexafluoropropylene copolymer) and Kel-F 800 (vinylidene fluoride-chlorotrifluoroethylene copolymer) based PEP formulations, and in the manufacture of Fluorel and/or Kel-F 800 based explosives molding powders or pyrotechnic materials extrusion feedstock. Extraction and recovery of TATB from PBX-9502 samples has been demonstrated on a laboratory scale using a carbon dioxide based process with some organic solvent. Although Viton-A (also vinylidene fluoride-hexafluoropropylene copolymer) was originally thought to be chemically equivalent to Fluorel, the desirable phase behavior found with Fluorel in SC CO<sub>2</sub> was not observed with the particular lot of Viton-A examined in this study even with the addition of polar cosolvent. A possible explanation could be that the Viton-A oligomers have different end-groups compared to Fluorel. This observation may illustrate the potential effects that slight modifications to a polymer may have on SC CO<sub>2</sub> solubility. Further study is required to gain better understanding of the fundamental chemical reasons for the observed behavior, and also to determine if other variants of Viton-A that are qualified for use in PEP materials may be soluble and thus processable in SC CO<sub>2</sub>.

Binder materials such as polyethylene, oxidized polyethylene, Estane 5702/5703, and cellulose acetate butyrate (CAB 381-20) do not appear to be amenable to SC CO<sub>2</sub> processing without either extreme temperatures or large amounts of organic cosolvents; however, further cosolvent work with these materials may be warranted. SC CO<sub>2</sub> fractionation work with CAB may be useful to investigate raw materials effects on LOVA gun propellant properties. Some variations of CAB that contain slightly modified chemical compositions might possibly be more amenable to SC CO<sub>2</sub> processing; however, this hypothesis requires further study.

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